In Situ Spectroscopy of Solvothermal Synthesis of Next-Generation Cathode Materials

Feng Wang, Jianming Bai

Brookhaven National Laboratory

Annual Merit Review and Peer Evaluation Meeting

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BAT #183

Overview

Timeline

- Start date: Oct., 2018
- End date: Oct., 2021
- Percent complete: 60%

Barriers

- Low energy density
- Cost
- Cycle life

Budget

- Total project funding
  - DOE 100%
- Funding received in FY19
  - 490 K
- Funding expected in FY20
  - 350 K

Partners

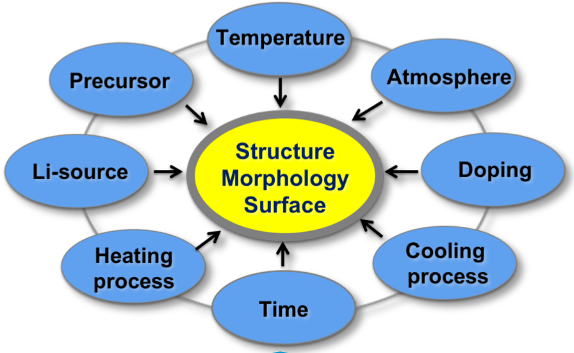
- Collaboration/interactions
  - Argonne National Lab
  - Lawrence Berkeley National Lab
  - Oak Ridge National Lab
  - Worcester Polytechnic Institute
  - Binghamton University
  - NEI Corporation

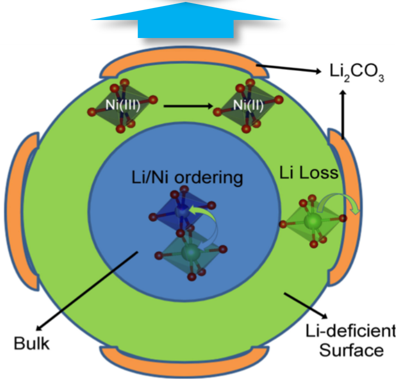
Relevance and Objectives

- **Develop synthetic protocols for preparing next-generation lithium ion cathode materials of improved performance at reduced cost.**

- Electrode performance, which is largely determined by the structural properties of active materials, can be advanced by
  - synthesis of phase-pure materials, *and*
  - control of their structure, morphology and surface *via* tuning synthesis parameters *(as exemplified)*.

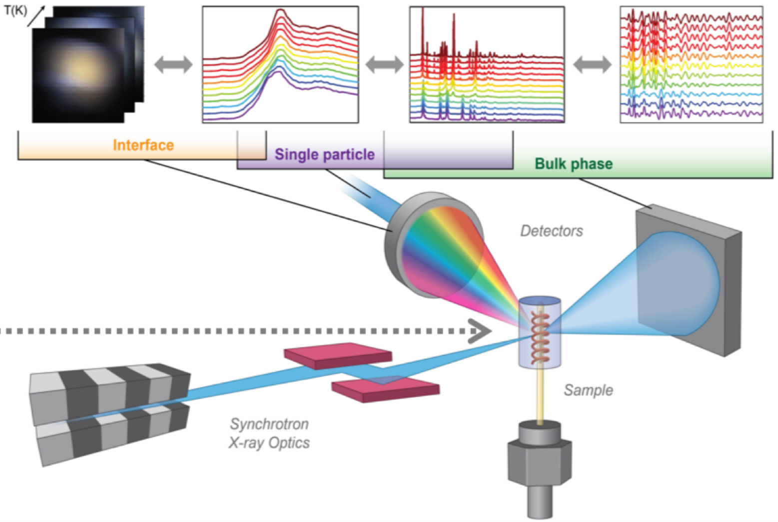
- Efforts in FY20 focus on high-Ni NMC ($LiNi_x(MnCo)_{1-x}O_2$; $x \geq 0.7$), aiming to address capacity fading-related issues:
  - structural disordering (*i.e.*, Li/Ni mixing)
  - surface instability (arising from Li loss/reconstructed surface layer; *as illustrated*).





Approach: *Synthesis by Design*

"black box"



***In situ* reactor**

Input for theory, modeling, scaled-up processing, …

BAT #054
#167
#402
#470

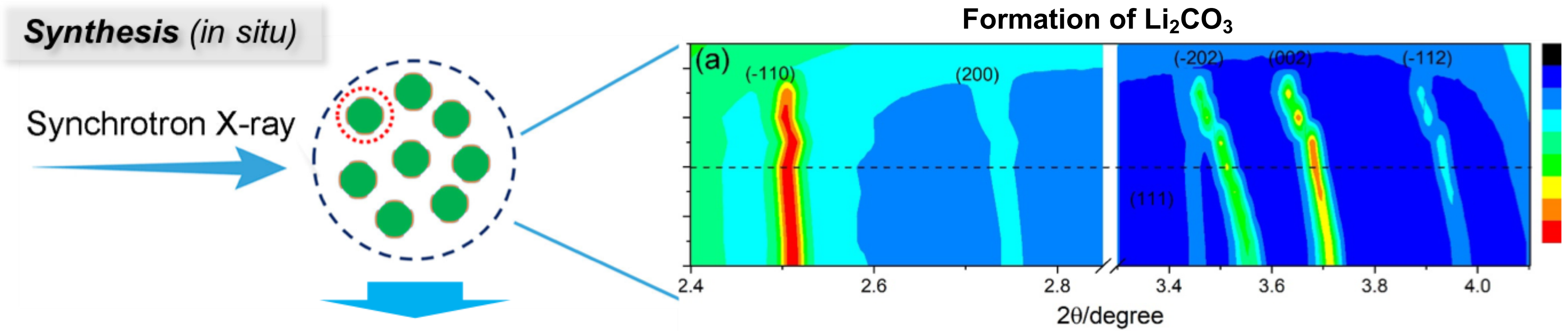
➢ Develop techniques for *in situ* characterization of synthesis and apply them to

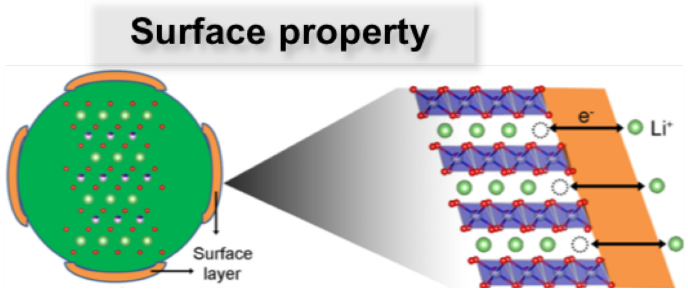
- identify reaction pathways and the involved intermediates
- determine reaction thermodynamics/kinetics under real synthesis condition
- thereby, design synthesis procedures (parameters) for improving materials performance and reducing cost (**in synergy W/ other efforts within the VTO program*).

Milestones

Time	**Description (*status*)**
Sept, 2019	Develop *in situ* techniques for tracking structural/chemical changes at particle surface during synthesis of high-Ni NMC. (*complete*)
Dec., 2019	Identify the impact of synthesis condition on the surface properties of high-Ni NMC. (*complete*)
March, 2020	Complete *in situ* study on the solid state synthesis of Ni-based cathode materials. (*complete*)
June, 2020	Complete *in situ* measurements of structural evolution during the sintering process in synthesis of NMC811 and NMC111 from hydroxide precursors – under ANL-BNL collaboration. (*in progress*)
Sept., 2020	Complete *in situ* characterization of local structural ordering in the core-shell structured NMC811. (*on track*)
Sept., 2020	Develop synthetic protocols for tailoring surface properties of high-Ni NMC. (*on track*)

Accomplishments: *In situ* techniques developed for tracking structural/chemical changes at particle surface during synthesis



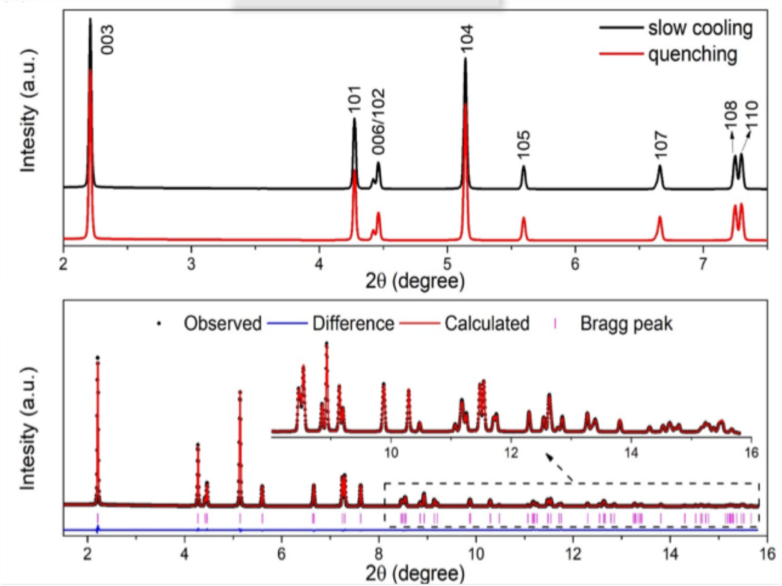


- High-flux X-rays: fast data acquisition and high sensitivity to minor phases, *such as*
  - Li_2CO_3 or other Li species that may impede Li^+ de-/intercalation at particle surface (*as illustrated; left*)

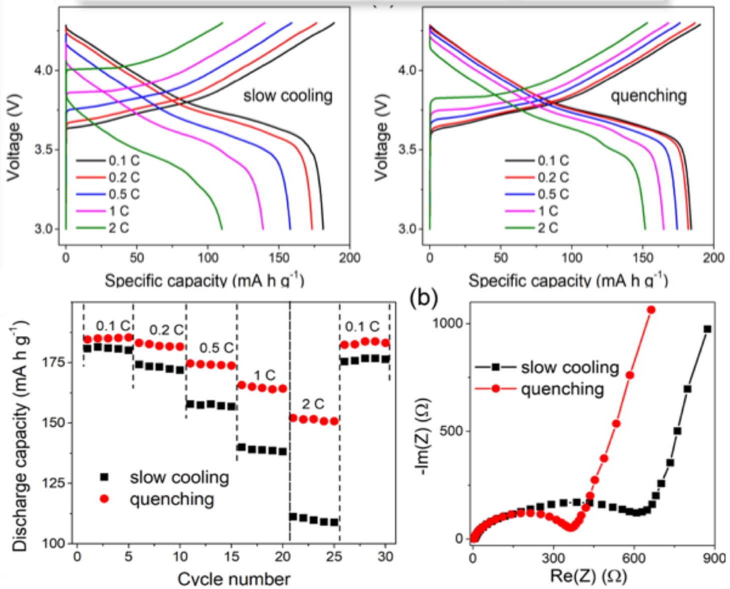
➢ *In situ* synchrotron-based techniques were developed, allowing detection of main phases as well as minor ones at surface as they form during synthesis.

Accomplishments: Identification of the impact of synthesis condition on the surface properties/performance of high-Ni NMC

***XRD**: structure*



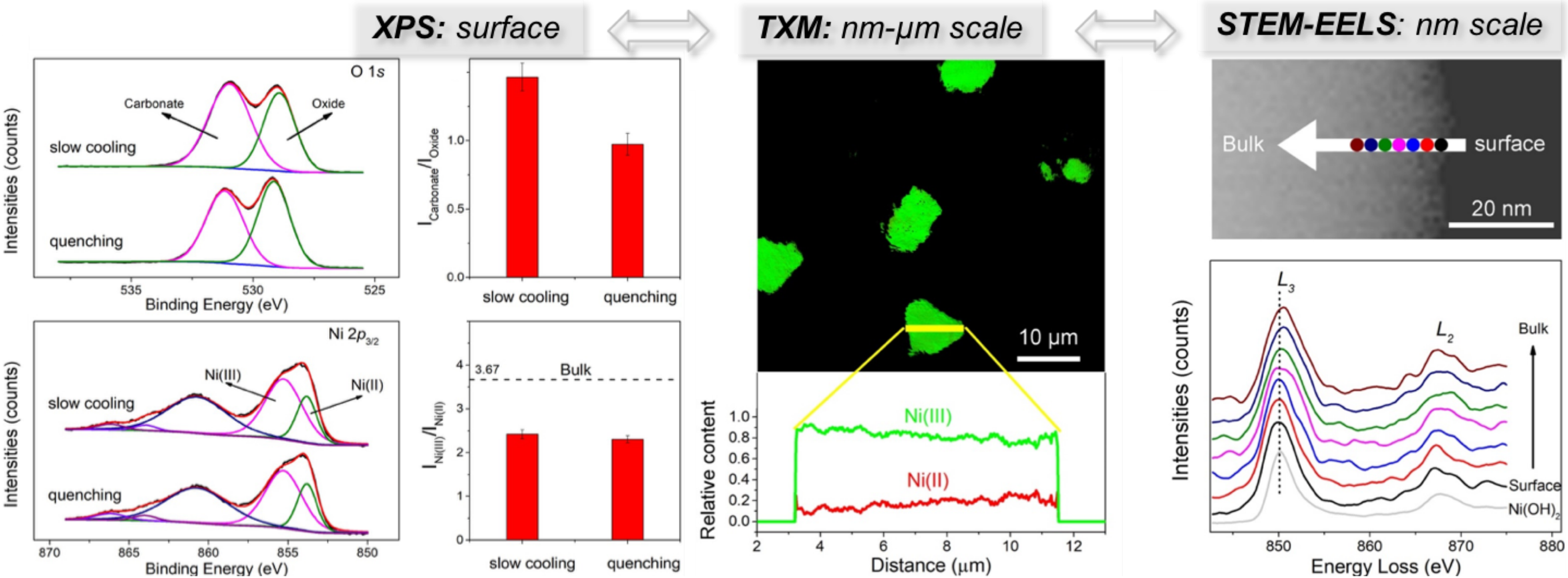
***Electrochemistry**: rate/impedance*



- ➢ Structural/electrochemical analysis of NMC71515 synthesized *via* slow cooling and quenching
  - similar structure in the two but high rate/low impedance in the sample by quenching
  - ➔ multiscale characterization *(*next two slides).*

M-J Zhang, et al., **Adv. Energy Mater.**, 9, 1901915 (2019).

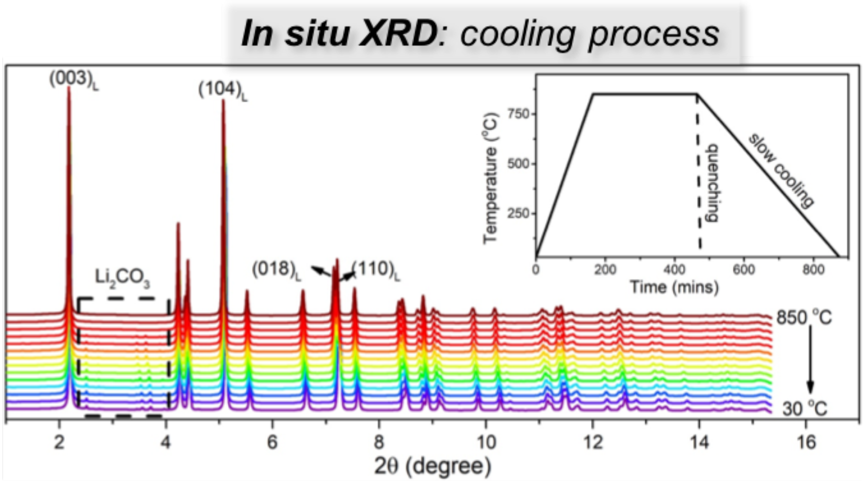
Multiscale chemical analysis across the surface and bulk

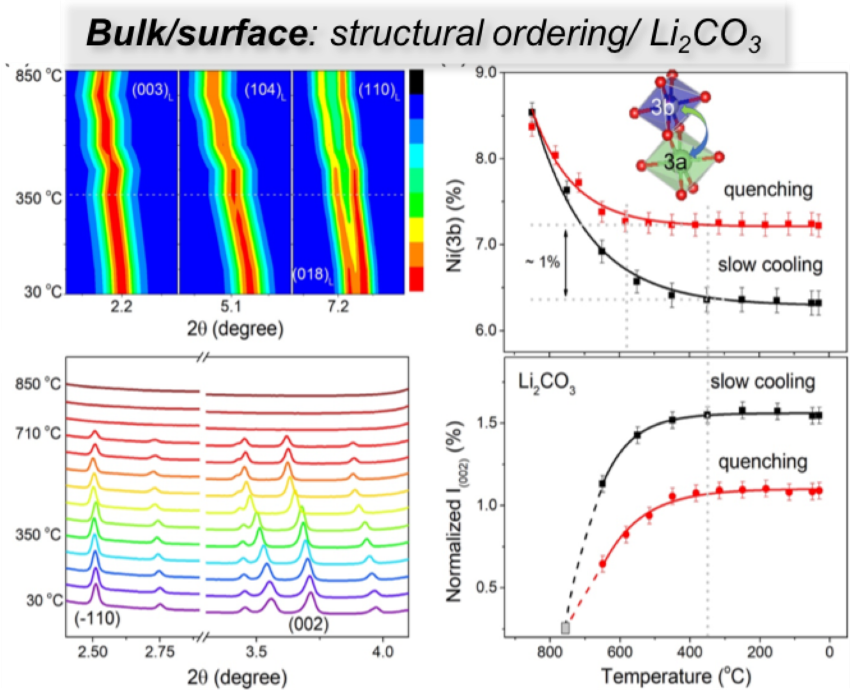


- Surface reconstruction in NMC71515:
  - accumulation of Li_2CO_3 at surface, reduction of Ni in the near-surface region
  - strong dependence on the cooling rate: less in the sample by quenching.

M-J Zhang, et al., **Adv. Energy Mater.**, 9, 1901915 (2019).

Tracking of changes in the bulk and surface upon cooling



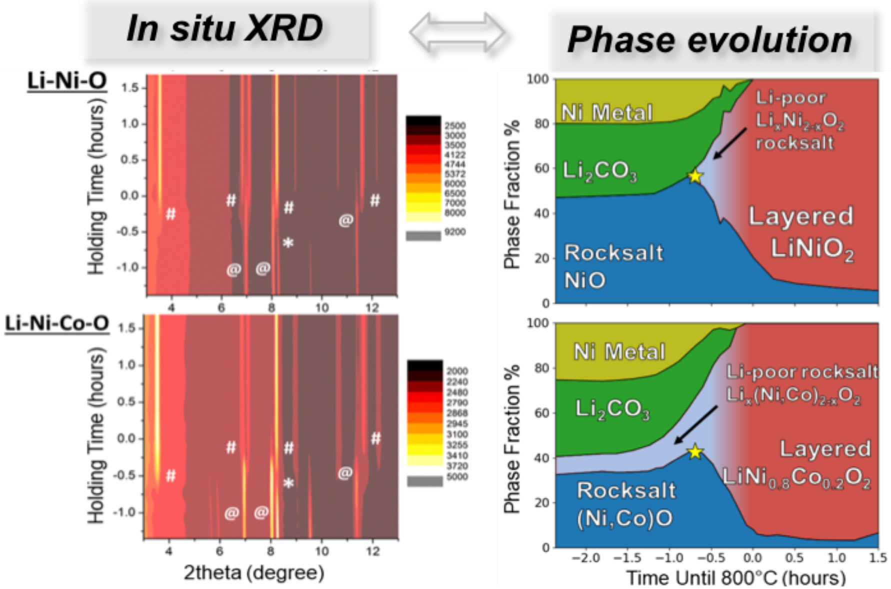


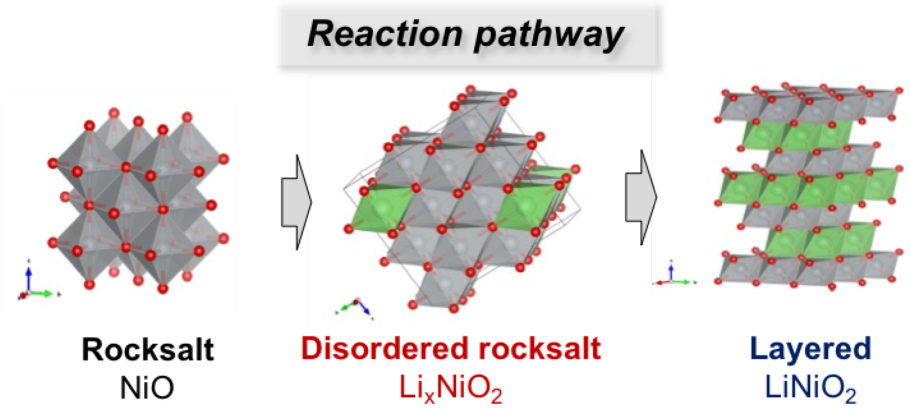
- Tracking of the synthesis process via *in situ* synchrotron XRD
  - structural ordering in the bulk
  - formation of Li_2CO_3 at the particle surface

➢ Surface reconstruction occurs during cooling, mostly at temperatures above 350 °C
  - greatly suppressed by quenching (compared to slow cooling)
  - mechanism: induced by Li/O loss from the near-surface region (see *Backup Slide 22*).

M-J Zhang, et al., **Adv. Energy Mater.**, 9, 1901915 (2019).

Accomplishments: Complete *in situ* study on the solid state synthesis of Ni-based cathode materials





- Rocksalt Ni(Co)O reacts with Li source to form a Li-poor disordered rocksalt intermediate, prior to the layered $LiNi(Co)O_2$ (see *Backup Slide 23*).

➢ Insights obtained from combined *in situ* and theory study, on the mechanistic origins of structural disordering in $LiNi(Co)O_2$, offer guidance to synthesis particularly in
- manipulating low-temperature intermediates towards target phases/structural properties.

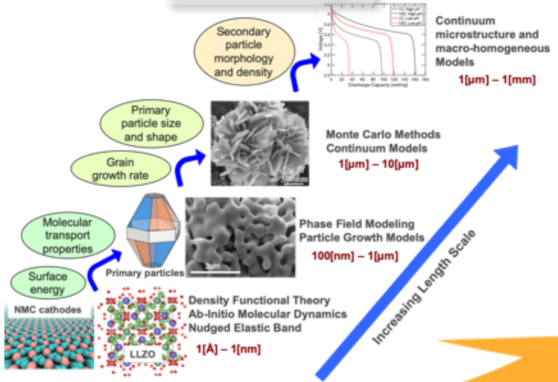
J. Bai, W. Sun, J. Zhao, D. Wang, P. Xiao, J.Y. Peter Ko, A. Huq, G. Ceder, F. Wang (*submitted*).

Accomplishments: ANL-BNL collaboration established within the Processing Science & Engineering Program

Lab-scale Processing

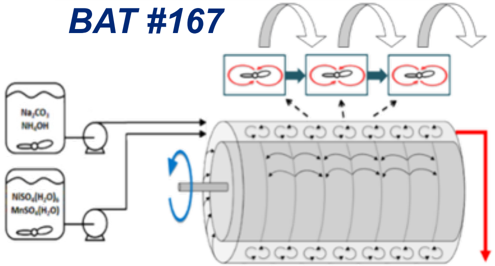
"Black box"

Modeling ***BAT #402***



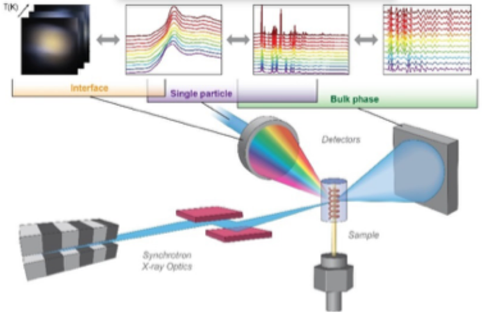
Scaled-up Processing

BAT #167



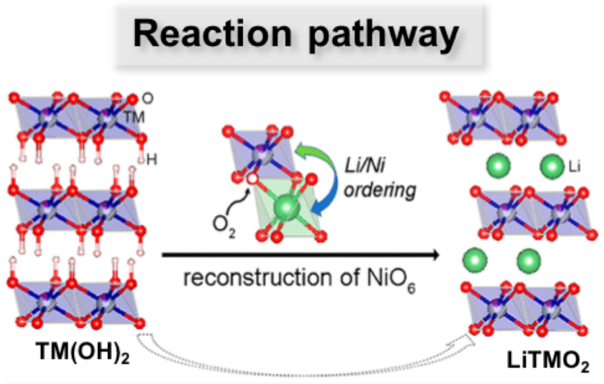
Taylor vortex reactor

***In situ* Study**

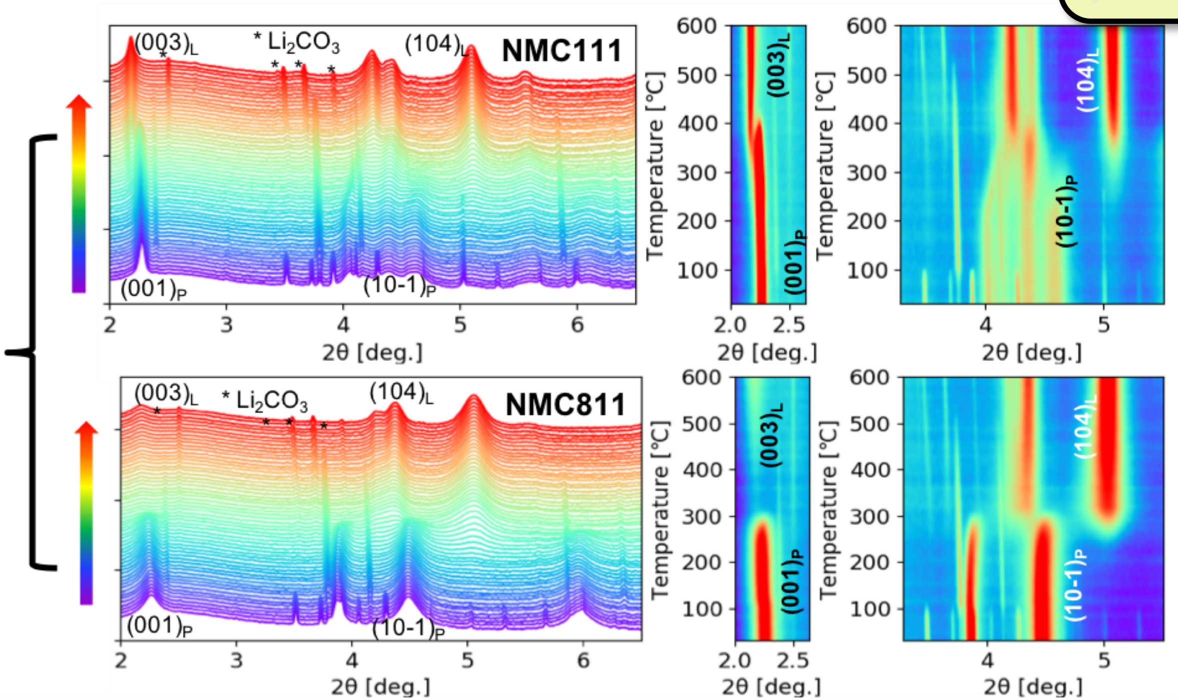


- **Traditional synthesis:** *trial & error*
- **Synthesis by design:** <u>modeling</u>, <u>*in situ* study</u> in synergy with <u>scaled-up processing</u>.

Reaction pathways during the sintering process in synthesis of NMC811 *vs.* NMC111

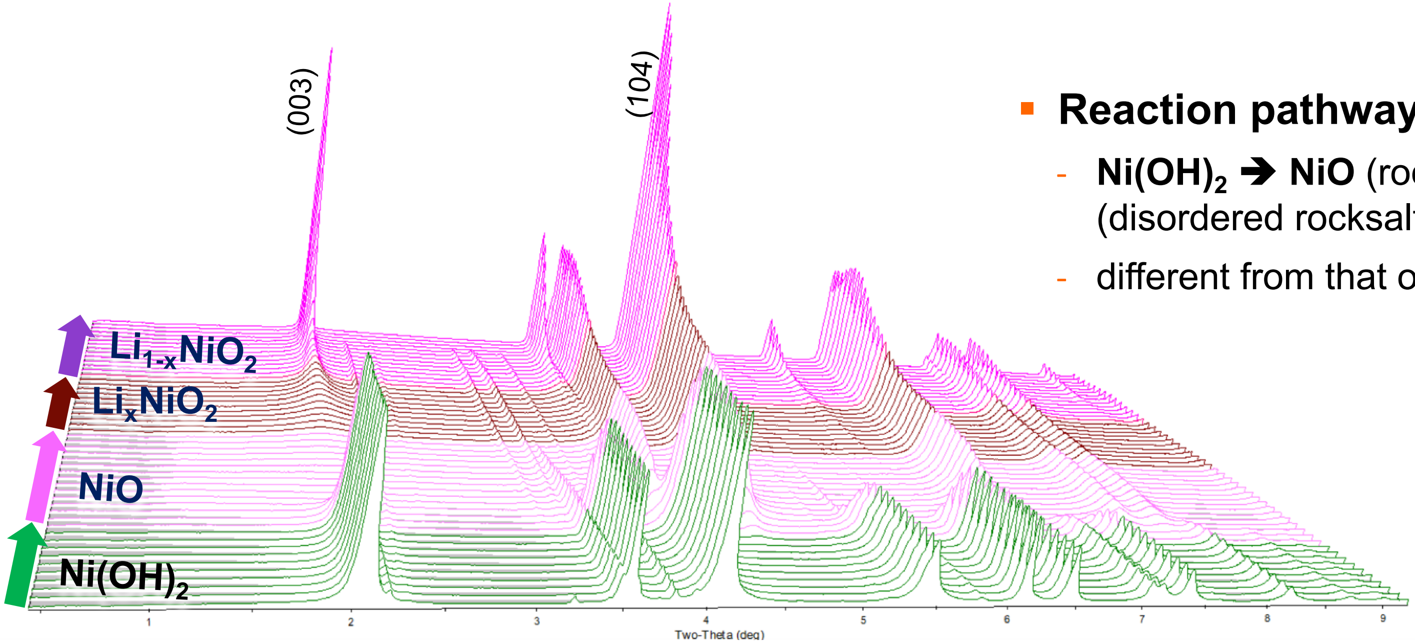


(J. Am. Chem. Soc. 140, 12484 (2018))



- **NMC111**: gradual transformation into the layered oxide with high structural ordering;
- **NMC811:** abrupt transformation/low ordering (see *Backup Slides 24-25: impact of atmosphere*).

Reaction pathways during the sintering process in synthesis of $LiNiO_2$ (*for comparison*)



- **Reaction pathway**
  - **$Ni(OH)_2$ ➔ NiO** (rocksalt) ➔ **Li_xNiO_2** (disordered rocksalt) ➔ **$Li_{1-x}NiO_2$** (layered)
  - different from that of NMC811/NMC111

➢ The reaction pathways and role of Mn/Co in tuning structural ordering were revealed, providing
- input for the <u>multiscale simulations</u> on structure-morphology evolution, *and also*
- guidance to <u>scaled-up processing</u> of high-Ni NMC cathode materials.

Response to Reviewers' Comments

We thank the four reviewers for their comments with great insights. Most of them are positive, so we only provide response to those ones with concerns and/or suggested new directions.

Comments	Response
One reviewer commented on the great potential of the technique in reducing cost and improving performance, and also suggested new experimental design with better statistics on composition and process, which may lead to better understanding of the variable space in composition/synthesis.	We have studied a large composition space (NMC111, NMC71515, NMC811, …, $LiNiO_2$) under different synthesis conditions (Slides 12-14, 17, 24-25), using solid-state, hydrothermal, microwave and other routes. We are now developing high-throughput, multimodal techniques for exploring larger composition/synthesis space.
One reviewer suggested to study the early-stage alloy formation and the corresponding nucleation/growth aspects and to consider as what the motivating factors are that drive phase formation and their relationship to the process condition. The reviewer also suggested to study synthesis under conditions that are different from those typically used.	We have extended our studies to early stage of the nucleation and growth during synthesis from hydroxides (*Slides 12-14, 26)*. And in response to the reviewer's 2nd comment on synthesis under different conditions, we have studied solid-state synthesis in the O_2, Air and Ar atmosphere (*Slides 24-25*), as well as different synthesis approaches (hydrothermal, microwave, …).
One reviewer recommended broadening collaboration with industrial for input outside the working team, to figure out what is commercially relevant.	We have extended our collaboration to industrial, currently using commercially relevant materials from companies as baseline samples, and will further broaden the industrial collaboration.
One reviewer suggested research on determining the local strain and depth-of-transition metal dissociation/dissolution, with potential input from DFT calculations.	We have been collaborating with CEDER group in Berkeley on DFT calculations (Slide 10), and will explore potential collaboration on the suggested studies.

Collaborations

- **Brookhaven National Lab** (*K. Chen-Wiegart, E. Dooryhee, S. Ehrlich, M. Ge, A. Kiss, W-K. Lee, L. Ma, J. Thieme, L. Wu, X. Xiao, Y. Zhu*)
  - Synchrotron X-ray and electron microscopy characterization of cathodes
- **Argonne National Lab** (D. *Abraham, K. Amine, P. Barai, Z. Chen, O. Kahvecioglu, K. Pupek, Y-H. Shin, C. Sun, Y. Ren, V. Srinivasan, X. Wang*)
  - Synthesis, characterization and modeling of high-Ni NMC and $LiNiO_2$ materials
- **Lawrence Berkeley National Lab** (*W. Sun, G. Ceder*)
  - Theoretical calculations and characterization of high-Ni NMC
- **Oak Ridge National Lab** (*A. Huq, J. Li, J. Liu*)
  - Neutron characterization of high-Ni NMC
- **Binghamton U.** (F. Xin, H. Zhou, *S. Whittingham*)
  - Synthesis and characterization of high-Ni cathodes
- **Worcester Polytechnic Institute** (P. Vanaphuti, Y. Wang)
  - Materials synthesis/characterization
- **NEI Corporation** (G. Skandan)
  - Baseline materials

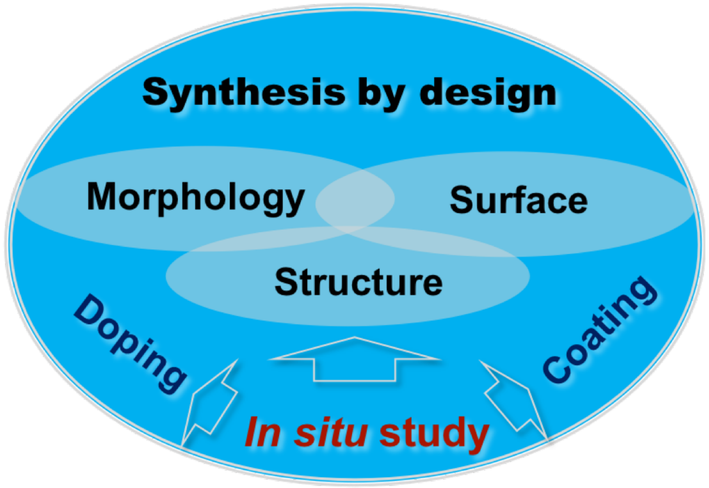
Remaining Challenges and Barriers

- **Main barriers:** Structural disordering has been one major obstacle (among others) to the commercial deployment of high-Ni NMC for lithium-ion batteries.
  - High-Ni loading is increasingly employed to boost Li-storage capacity while reducing cost but, on the other hand, brings issues of structural disordering, *i.e.*, Li/Ni mixing and surface reconstruction (involving Li loss/reconstructed surface layer) that are detrimental to performance.
- **Technical challenges:** Synthesis of high-Ni NMC with intended control of structural ordering is yet to be established, largely due to the challenges associated with
  - the complexity of synthesis reaction under *non-equilibrium* condition;
  - high sensitivity of the structural ordering, in the bulk and surface, to synthesis parameters.

➢ Some of the barriers/challenges may be tackled via *synthesis by design,* empowered by the combined *in situ* study and multiscale simulation.

Future Work (*FY20-21*)

- Continue efforts on synthesis of high-Ni NMC by design aided by *in situ* study, with the focus on:
  - impact of the high Ni content (≥ *80%)* on structural ordering and surface properties
  - combined in *situ* study/multiscale simulation on the structure-morphology evolution through ANL-BNL collaboration (*see Slide 18 and Backup Slide 26*)
  - new synthesis routes, combined with doping/coating where possible, to gain control of the structure, morphology and surface (*as illustrated*)

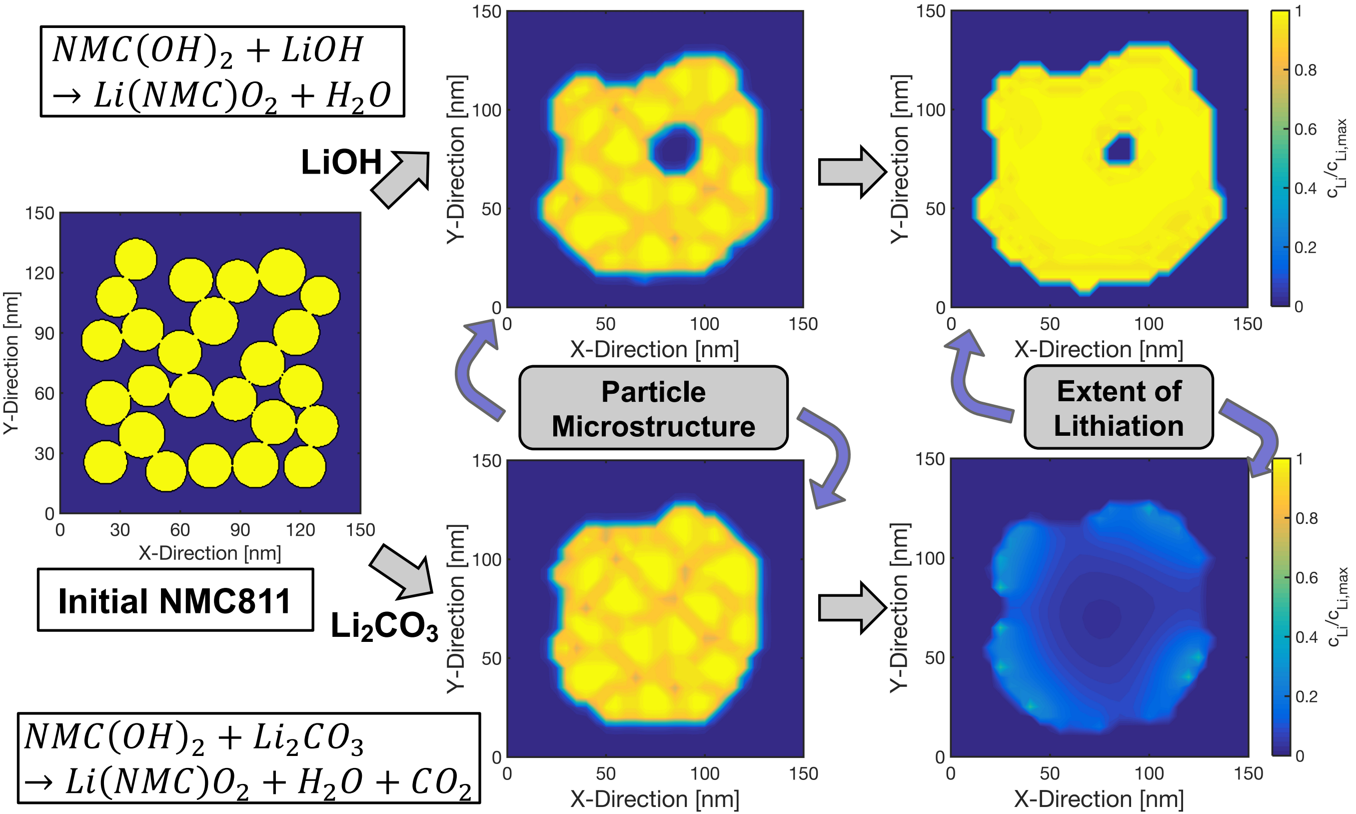


- Develop new *in situ* techniques/capabilities:
  - suited to studying different types of synthesis
  - allowing multiscale/multimodal characterization of structure, morphology and surface
  - with high resolution/sensitivity to local structural/chemical ordering
- Apply the established approaches to synthesis of low-Co/Co-free cathodes and other types of cathode/anode materials.

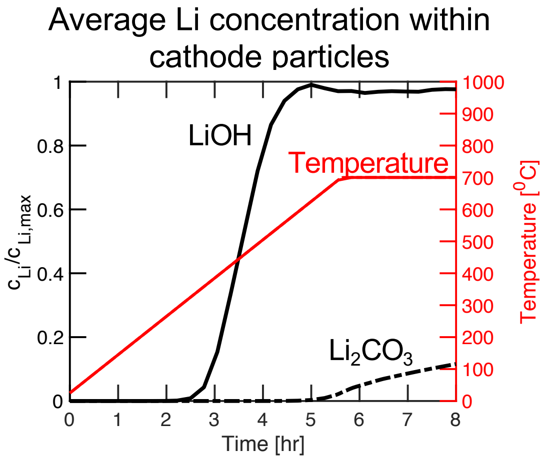
Any proposed future work is subject to change based on funding levels

ANL-BNL collaboration: Multi-scale simulations/*in situ* study on microstructure evolution (*results from P. Barai/V. Srinivasan; *BAT #402*)

$$NMC(OH)_2 + LiOH \rightarrow Li(NMC)O_2 + H_2O$$



$$NMC(OH)_2 + Li_2CO_3 \rightarrow Li(NMC)O_2 + H_2O + CO_2$$



- Higher melting temperature of Li_2CO_3 prevents it from reacting with NMC811 at low temperatures.
- **Reaction rate constants for lithiation are the input parameters incorporated from *in situ* XRD analysis.**

Any proposed future work is subject to change based on funding levels

Summary

- **Relevance/Objective:** Develop synthetic protocols for preparing Li-ion cathode materials of improved performance at reduced cost.
- **Approach:** synthesis by design aided by *in situ* study
- **Accomplishments:** (*all milestones were met or exceeded*)
  - New *in situ* techniques were developed and applied to studies of the synthesis in preparing a series of high-Ni NMC with varying composition/precursor/atmosphere, whereby unveiling mechanistic origins of structural disordering and surface reconstruction in such materials.
  - Future work was planned to tackle some of the remaining barriers/challenges for commercial deployment of high-Ni NMC; related activities have already been initiated, as demonstrated by preliminary results from this project and/or from collaborations.
- **Technical highlights:** (*demonstrated great synergy within the VTO program*)
  - Insights obtained from this project not only offer guidance to synthesis of high-performance cathode materials but also provide input for theory, modeling and scaled-up processing within the VTO program (and beyond).
  - The developed capabilities/approaches may be applied broadly for synthesis of various cathode/anode materials by design.

Acknowledgement

- Support from the U.S. Department of Energy's Office of Vehicle Technologies (Program Manager: Peter Faguy)
- Contributions by team members and collaborators

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Worcester Polytechnic Institute
Panawan Vanaphuti
Yan Wang

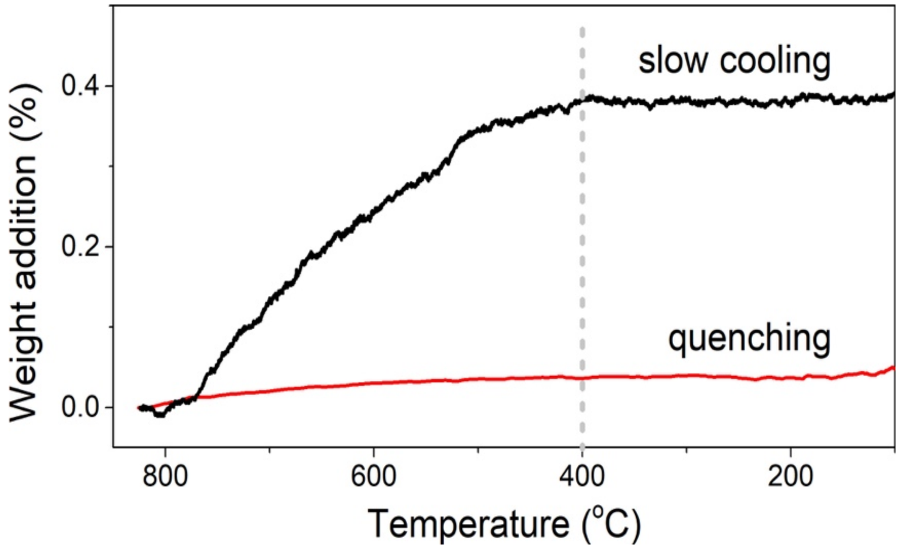
Binghamton University
F. Xin
Hui Zhou
Stan Whittingham

NEI Corporation
Ganesh Skandan

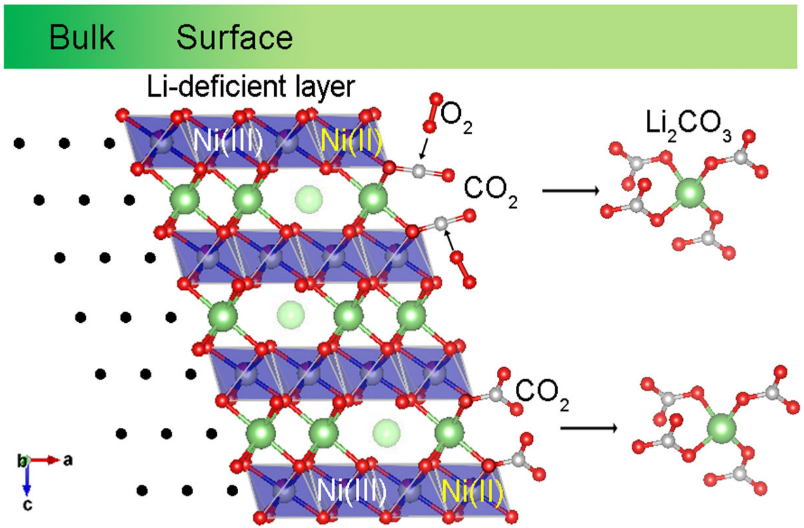
Technical Backup Slides

Backup (1) Cooling-induced surface reconstruction

TGA analysis on the mass change:

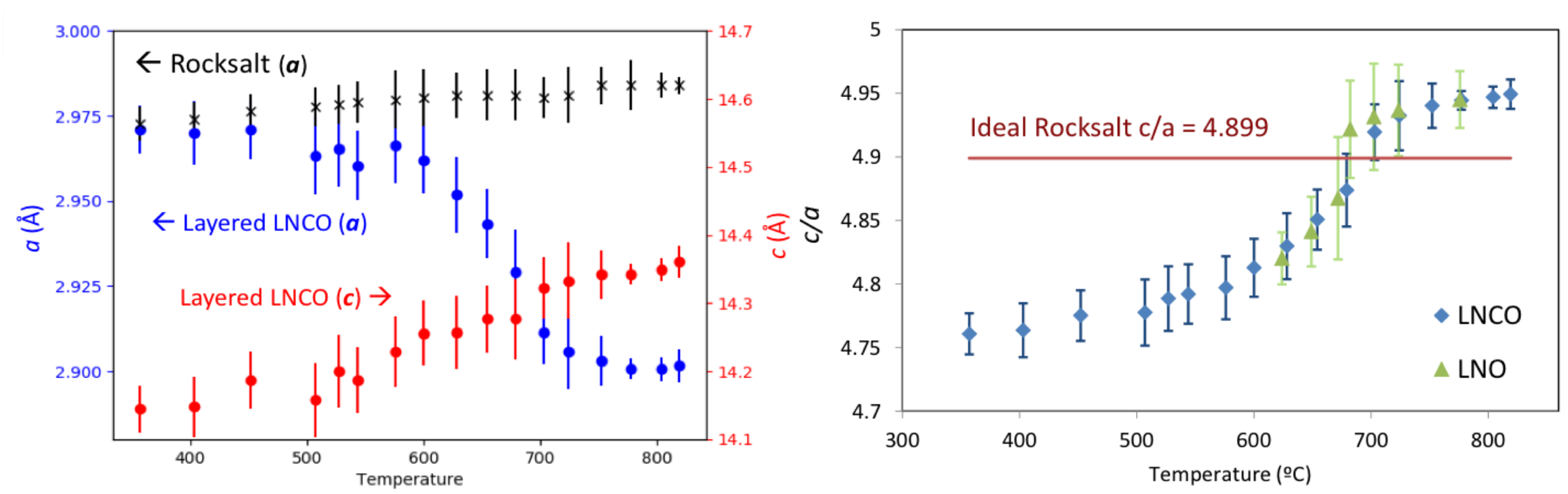


Proposed mechanisms:



- Surface reconstruction is induced by Li/O from the near-surface region upon cooling, which can be greatly suppressed by quenching.

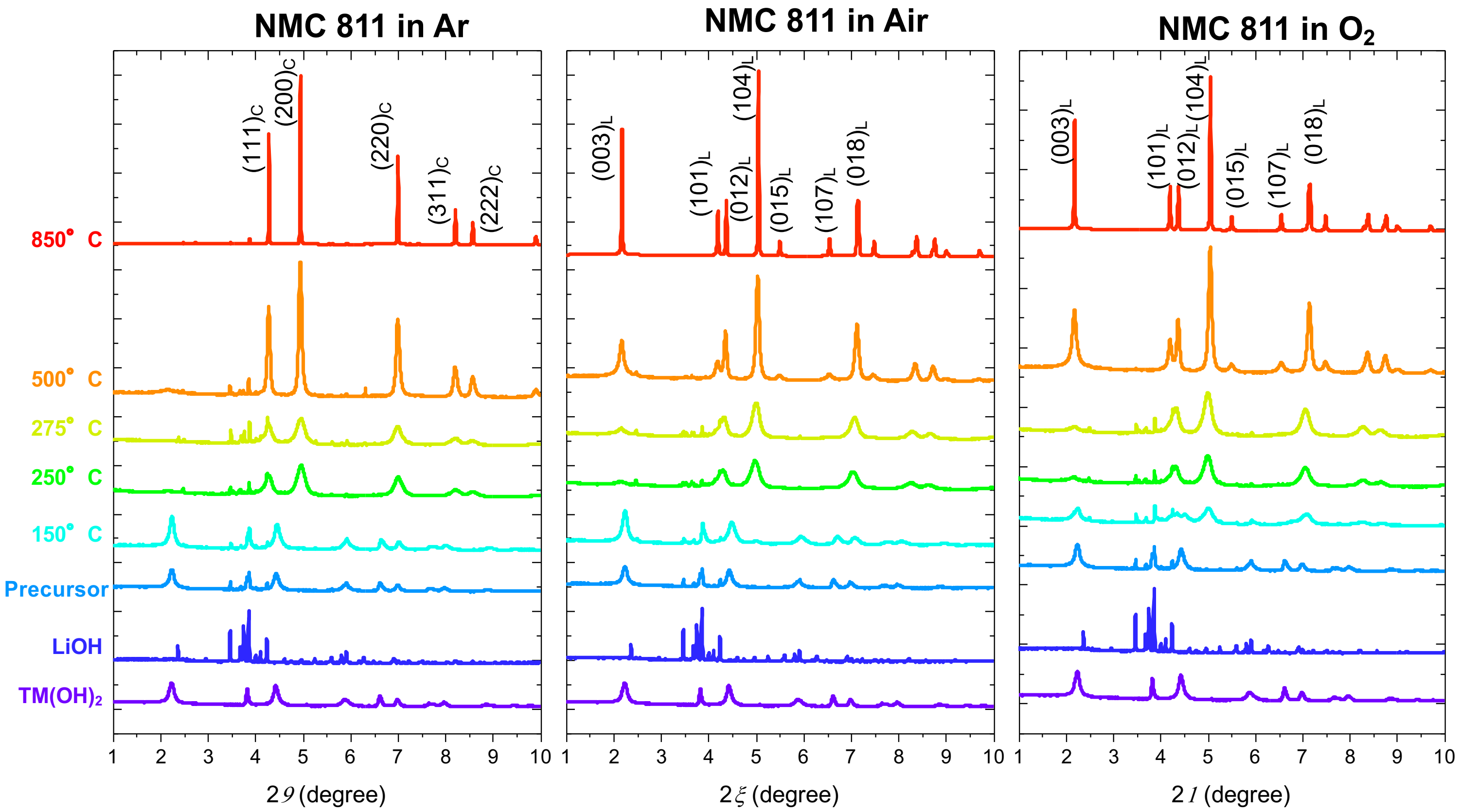
Backup (2) Synthesis pathways of the layered $LiNi(Co)O_2$



- Measured lattice parameters *a, c* with XRD indicate the deviation of the aspect ratio *c*/*a* to 4.899 (or 2√6) in the intermediate structures of Li-deficient $Li_xNi_{1-x}O_2$ (LNO) and $Li_x(Ni_{0.8}Co_{0.2})_{1-x}O_2$ (LNCO).

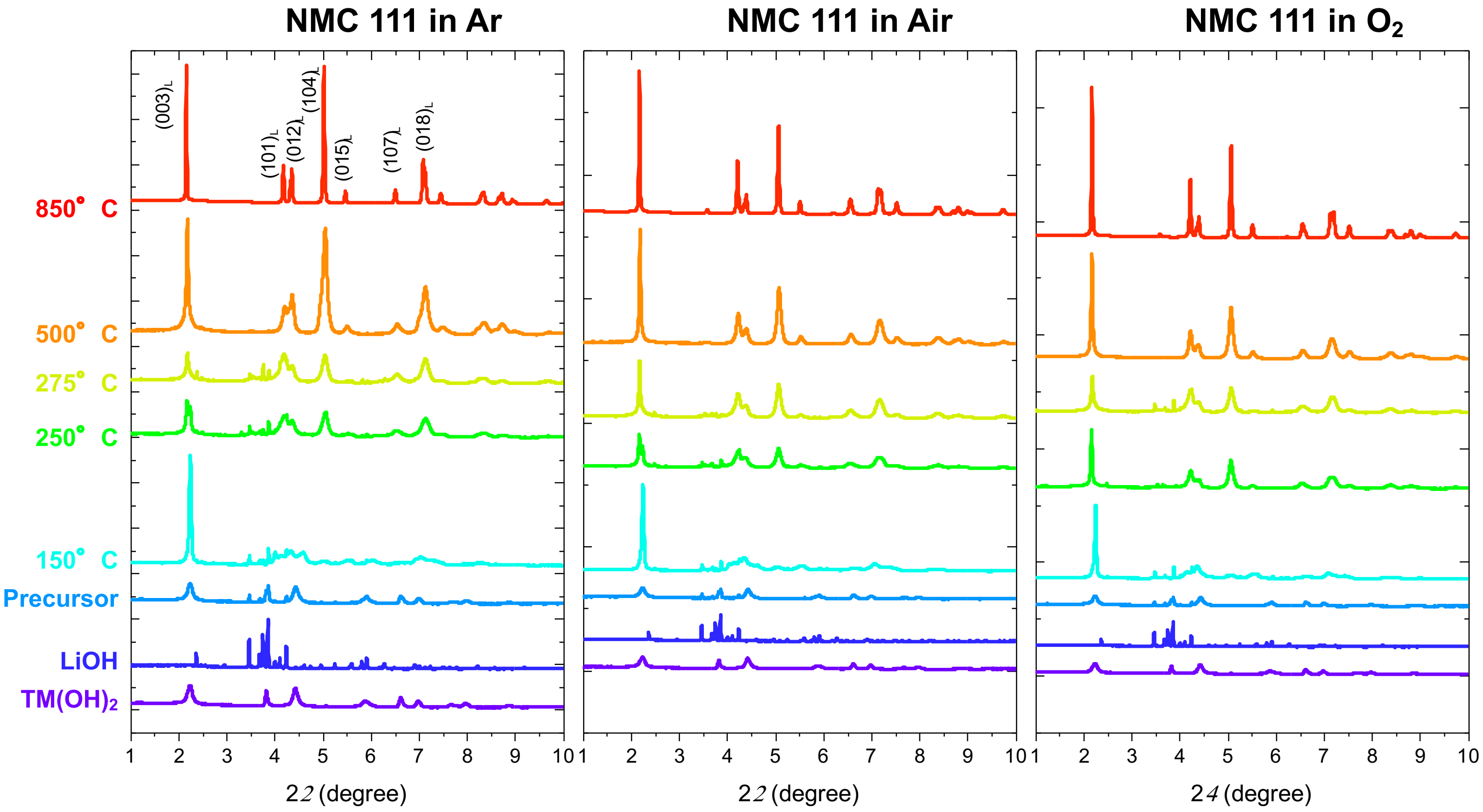
➢ Formation of the disordered rocksalt prior to formation of the layered $LiNi(Co)O_2$.

Backup (3) Synthesis of NMC811 in different atmospheres



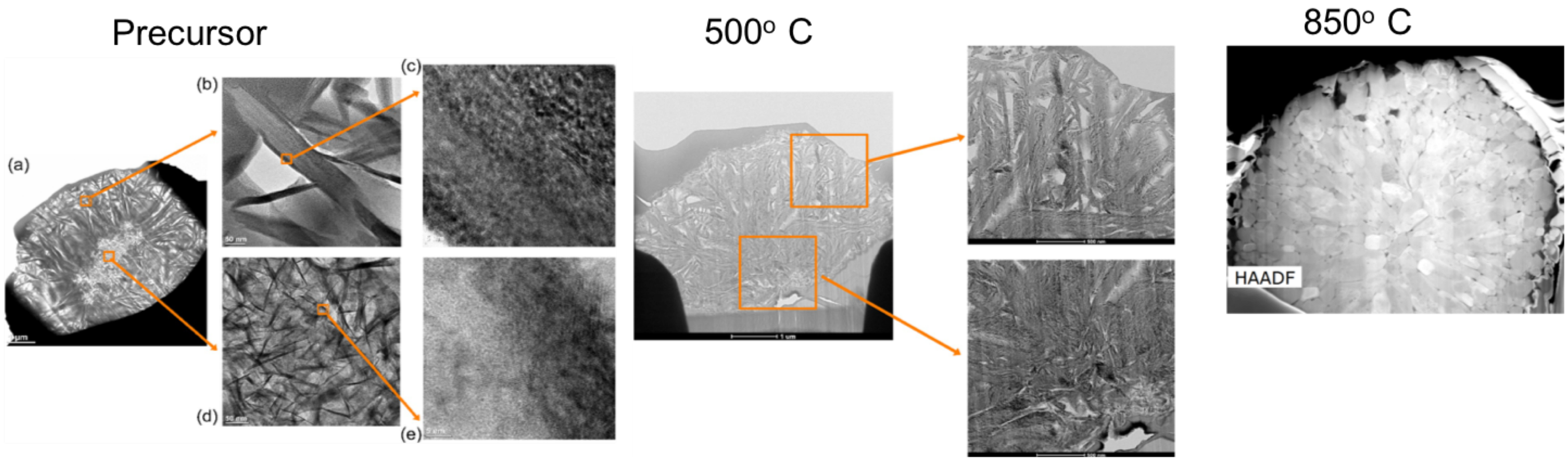
- ➢ **Oxidation environment needed for oxidizing Ni during synthesis of NMC811.**

Backup (4) Synthesis of NMC111 in different atmospheres



- **Oxidation environment: NOT necessary for synthesis of NMC111.**

Backup (5) Particle growth /microstructure evolution in NMC811



- Cross-section TEM of the precursor/NMC811 synthesized at different temperatures
  - particle growth during sintering
  - microstructure change from flake-like to spherical particles

➢ Future work: *in situ* experimentation/multiscale simulations on the particle growth and microstructure evolution (*through ANL-BNL collaboration*).